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Some rhenium hydride complexes with tetradentate phosphine co-ligands: the crystal structure of $\mathrm{Re(H_2BEt_2)}$(*racemic*-tetraphos)

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Abstract

$\mathrm{ReH_5(PMePh_2)_3}$ reacts with $\mathrm{P(CH_2CH_2PPh_2)_3}$ ($\mathrm{PP_3}$) in the absence of solvent at 180°C to give $\mathrm{ReH(PMePh_2)(PP_3)}$. Under similar conditions, $\mathrm{ReCl_3(PMePh_2)_3}$ reacts with tetraphosphine ligands $\mathrm{PP_3}$ or commercially available $\mathrm{P_4}$ ($\mathrm{Ph_2PCH_2CH_2P(Ph)CH_2CH_2P(Ph)CH_2CH_2PPh_2}$) to produce $\mathrm{ReCl_3(PP_3)}$ and $\mathrm{ReCl_3(P_4)}$, respectively. Treatment of $\mathrm{ReCl_3(PP_3)}$ with $\mathrm{NaBH_4}$ yielded $\mathrm{ReH_3(PP_3)}$, which is converted into $\mathrm{[ReH_4(PP_3)]^+}$ when protonated. Treatment of $\mathrm{ReCl_3(P_4)}$ with $\mathrm{NaBH_4}$ in MeOH/benzene produced a mixture of $\mathrm{ReH_3}$(*meso*-$\mathrm{P_4}$) and $\mathrm{ReH_3}$(*rac*-$\mathrm{P_4}$). On the other hand, a mixture of $\mathrm{ReH_3}$(*meso*-$\mathrm{P_4}$) and the novel complex $\mathrm{Re(BH_2Et_2)}$(*rac*-$\mathrm{P_4}$) was obtained when $\mathrm{ReCl_3(P_4)}$ was treated with an old sample of $\mathrm{LiBHEt_3}$ (actually containing $\mathrm{LiBEt_4/LiBH_2Et_2}$) in THF. Protonation of $\mathrm{ReH_3}$(*meso*-$\mathrm{P_4}$) produced $\mathrm{[ReH_4}$(*meso*-$\mathrm{P_4})]^+$. The T_1 values of the hydride resonances of the hydride complexes suggested that all are classical rhenium hydride complexes as the Re centres are too basic to form η^2-dihydrogen complexes. $\mathrm{Re(H_2BEt_2)}$(*rac*-$\mathrm{P_4}$) crystallized in the space group $C2/c$ with cell parameters $a = 17.651(3)$, $b = 13.874(2)$, $c = 17.694(4)$ Å, $\beta = 102.22(2)°$, $V = 4235(3)$ Å^3, $Z = 4$, $R = 0.028$ and $R_w = 0.029$ for the 3343 reflections with $I > 3\sigma(I)$. The $\mathrm{BH_2Et_2^-}$ unit is bound to rhenium via the two bridging hydrides.

1. Introduction

There has been renewed interest in the chemistry of rhenium polyhydride complexes containing tertiary phosphines [1], particularly because they exhibit a variety of interesting structural types and unusual chemical reactivity. A large number of rhenium polyhydride complexes of monodentate and bidentate ancillary ligands are known [2,3]. However, examples of rhenium polyhydride complexes containing polydentate phosphines are still quite rare. The advantages of chelating polyphosphines have been discussed [4]. Wojcicki *et al.* have reported several rhenium hydride complexes of Cyttp (Cyttp = $\mathrm{PhP(CH_2CH_2CH_2PCy_2)_2}$) [5]. Crabtree *et al.* have recently reported the preparation and spectroscopic data of $\mathrm{ReH_5(PP_2)}$ and $\mathrm{[ReH_6(PP_2)]^+}$ ($\mathrm{PP_2} = \mathrm{PhP(CH_2CH_2PPh_2)_2}$ [6]) and $\mathrm{ReH_5(NP_2)}$ and $\mathrm{[ReH_6(NP_2)]^+}$ ($\mathrm{NP_2} = \mathrm{HN(CH_2CH_2PPh_2)_2}$ [7]). We report here the synthesis and characterization of some rhenium hydride complexes containing the tetradentate phosphines $\mathrm{P_4}$ ($\mathrm{P_4} = \mathrm{Ph_2PCH_2CH_2P(Ph)CH_2CH_2P(Ph)CH_2CH_2PPh_2}$, also known as tetraphos-1) and $\mathrm{PP_3}$ ($\mathrm{PP_3} = \mathrm{P(CH_2CH_2PPh_2)_3}$, also know as tetraphos-2). We are particularly interested to compare the structures of neutral complexes $\mathrm{ReH_3}$(*meso*-$\mathrm{P_4}$), $\mathrm{ReH_3}$(*rac*-$\mathrm{P_4}$) and $\mathrm{ReH_3(PP_3)}$ which are not expected to have H–H interactions with the iso-electronic cationic complexes $\mathrm{[Os(H_2)(H)}$(*meso*-$\mathrm{P_4})]^+$ [8], and $\mathrm{[M(H_2)(H)(PP_3)]^+}$, M=Fe, Ru which do have H–H bonding [9–11]. We have measured the variable temperature values of the T_1 of the hydrides on rhenium to probe the possibility of H–H interactions.

2. Experimental details

2.1. General

Unless otherwise noted, all manipulations were done in an Ar or $\mathrm{N_2}$ atmosphere by use of Schlenk techniques. Solids were handled in a Vacuum Atmosphere drybox filled with $\mathrm{N_2(g)}$. All solvents were dried over appropriate drying reagents and distilled under $\mathrm{N_2}$ before use. Reagent-grade chemicals were used as purchased from Aldrich Chemical Company, Inc. unless otherwise stated. Phosphines ligands were purchased

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from Strem Chemical Co. or Digital Specialty Chemicals Ltd. $ReCl_3(PMePh_2)_3$ [12] and $ReH_5(PMePh_2)_3$ [13] were prepared as described in the literature for analogous compounds.

NMR spectra were obtained on a Varian XL 400, operating at 400.00 MHz for ^1H, 161.98 MHz for ^{31}P, or on a Varian XL 200 operating at 200.00 MHz for ^1H, 80.98 MHz for ^{31}P. Chemical shifts refer to room temperature conditions unless specified otherwise. All ^{31}P NMR were proton decoupled. ^{31}P chemical shifts were measured relative to ~1% $P(OMe)_3$ in C_6D_6 sealed in coaxial capillaries and are reported relative to H_3PO_4 by use of $\delta(P(OMe)_3) = 140.4$ ppm. ^1H chemical shifts were measured relative to partially deuterated solvent peaks, but are reported relative to tetramethylsilane. T_1 times were measured by use of the inversion recovery method. Microanalyses were performed by the Canadian Microanalytical Service, Ltd.

2.2. Synthesis of $ReH(PMePh_2)(PP_3)$ (1)

A mixture of 0.15 g of $ReH_5(PMePh_2)_3$ (0.19 mmol) and 0.15 g of PP_3 (0.22 mmol) was heated at *ca.* 180°C for 2 h. The reaction mixture was cooled down to room temperature, and 3 ml of EtOH were added. The resulting mixture was stirred overnight to give a bright yellow precipitate. The precipitate was collected by filtration, washed with EtOH, and dried *in vacuo* overnight. ^{31}P NMR (C_6H_6/C_6D_6): δ 133.6 (br d, $J(PP) = 152.4$ Hz); 42.5 (br d, $J(PP) = 9.1$ Hz); 41.7 (br d, $J(PP) = 14.6$ Hz); −6.9 (dm, $J(PP) = 152.4$ Hz). ^1H NMR (C_6D_6): δ −8.39 (m, ReH); 1.1–2.6 (m, CH_2, CH_3); 6.6–8.2 (m, Ph).

2.3. Synthesis of $ReH_3(PP_3)$ (2)

A mixture of 0.62 g of $P(CH_2CH_2PPh_2)_3$ (0.93 mmol) and 0.81 g of $ReCl_3(PMePh_2)_3$ (0.91 mmol) was heated without solvent at *ca.* 200°C for 2 h. The reaction mixture was then cooled down to room temperature, and 15 ml of EtOH were added to the reaction flask. The resulting mixture was stirred overnight to give a bright yellow solid. The solid was collected by filtration, washed with EtOH, and dried *in vacuo* to give 0.53 g (61% yield) of $ReCl_3(PP_3)$. The $ReCl_3(PP_3)$ was then suspended in 20 ml of benzene and 10 ml of EtOH. To the reaction flask was added 0.10 g of $NaBH_4$ (2.64 mmol). The reaction mixture was then refluxed for 2 h to give a yellow solution and some precipitate. The precipitate was removed by filtration and washed with benzene. The solvents from the filtration and the washing were removed completely, and 8 ml of EtOH were added to the residue to give a light yellow powder. The powder was collected by filtration, washed with EtOH, and dried *in vacuo.* Yield: 0.31 g, 40% based on $ReCl_3(PMePh_2)_3$ or 65% based on $ReCl_3(PP_3)$. $^{31}P\{^1H\}$ NMR (C_6H_6/C_6D_6): δ 156.9 (q, $J(PP) = 33.7$ Hz, central phosphorus); 68.1 (d, $J(PP)) = 33.7$ Hz, terminal phosphorus). ^1H NMR (C_6D_6): δ −6.48 (td, $J(PH) = 12.7$, 4.0 Hz, ReH); 1.2–1.4 (m, 6 H, CH_2); 1.9–2.1 (m, 6 H, CH_2); 7.0 (br, 18 H, Ph); 7.8 (br, 12 H, Ph). Anal. Found: C, 59.44; H, 5.13. $C_{42}H_{45}P_4Ru$ calcd.: C, 58.67; H, 5.28%.

2.4. Synthesis of $[ReH_4(PP_3)]BF_4$ (3)

To a suspension of 0.10 g of **2** (0.12 mmol) in 15 ml of Et_2O was added 2 drops of $HBF_4 \cdot Et_2O$ to give a light purple solid. After the reaction mixture was stirred for an additional 15 min, the solid that formed was collected by filtration, washed with Et_2O and dried *in vacuo*. Yield: 0.10 g, 91%. ^{31}P NMR(acetone/C_6D_6): δ 132.8 (q, $J(PP) = 17.2$ Hz, central phosphorus); 48.9 (d, $J(PP) = 17.2$ Hz, terminal phosphorus). ^1H NMR (CD_2Cl_2); δ −6.25 (qd, $J(PH) = 11.7$, 5.1 Hz ReH); 2.60 (d, $J(PH) = 16.4$, 12 H, CH_2); 7.0–7.4 (m, 30 H, Ph). Anal. Found: C, 53.03; H, 4.89. $C_{42}H_{46}BF_4P_4Re$ calcd.: C, 53.23; H, 4.89%.

2.5. Synthesis of $ReCl_3(meso\text{-}P_4)$ and $ReCl_3(rac\text{-}P_4)$

A mixture of 1.20 g of $ReCl_3(PMePh_2)_3$ (1.34 mmol) and 1.0 g of commercial P_4 (1.49 mol) was heated without solvent at *ca.* 200°C for 3 h in an evacuated flask. The reaction mixture was then cooled down to room temperature. Addition of MeOH to the residue produced a yellow-greenish solid which was insoluble in common organic solvents. The solid was collected by filtration, washed with MeOH, and dried *in vacuo.* Yield: 0.80 g, 67%.

2.6. Synthesis of $ReH_3(meso\text{-}P_4)$ (4) and $Re(H_2BEt_2)(rac\text{-}P_4)$ (5)

The mixture of trichlorides just described (0.80 g, 0.83 mmol) was suspended in 30 ml of THF. To the above suspension was added 4 ml of 1 M "$LiBHEt_3$" [14*] in THF (4 mmol). The reaction mixture was stirred at room temperature overnight to give a yellow solution. MeOH (2 ml) was then added to the reaction flask to neutralize the unreacted "$LiBHEt_3$". The solvent was removed completely *in vacuo.* The residue was extracted with *ca.* 100 ml Et_2O to give a yellow solution. The Et_2O insoluble residue was extracted with *ca.* 30 ml of CH_2Cl_2 to give a yellow solution. The Et_2O extract was evaporated and the resulting residue was washed with MeOH to give a yellow powder. The powder was collected by filtration, washed with MeOH, and dried *in vacuo* to give 0.42 g (58% of **4** based on

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* Reference number with asterisk indicates a note in the list of references.

$ReCl_3(P_4)$ or 39% of **4** based on $ReCl_3(PMePh_2)_3$). ^{31}P NMR (C_6H_6/C_6D_6): δ 100.6 (s, central PPh); 56.0 (s, terminal PPh_2). ^1H NMR (C_6D_6): δ -6.86 (tt, J(PH) = 17.2, 5.4 Hz, ReH); 0.9–2.2 (m, 12 H, CH_2); 6.9–8.3 (m, 30 H, Ph). Anal. Found: C, 58.64; H, 5.64. $C_{42}H_{45}P_4Re$ calcd. C, 58.67; H, 5.28%.

The CH_2Cl_2 extract was evaporated completely and the residue was washed with MeOH to give a yellow solid. The solid was collected by filtration, washed with MeOH, and dried *in vacuo* to give 0.20 g of **5**, or a yield of 26% based on $ReCl_3(P_4)$ or 17% based on $ReCl_3(PMePh_2)_3$. ^{31}P NMR (C_6H_6/C_6D_6): δ 81.5 (s, central PPh); 51.5 (s, terminal PPh_2). ^1H NMR (C_6D_6): δ -7.25 (br, ReH); 0.88 (t, J(HH) = 7.3 Hz, 6 H, CH_3); 1.1–2.0 (m, 16 H, CH_2); 6.9–7.8 (m, 30 H, Ph). Anal. Found: C, 58.91; H, 6.01. $C_{46}H_{54}BP_4Re$ calcd.: C, 59.55; H, 5.87%.

2.7. Synthesis of ReH_3(meso-P_4) (4) and ReH_3(rac-P_4) (6)

The mixture of trichlorides described above (0.4 g, 0.4 mmol) was suspended in a mixture of MeOH (10 ml), benzene (20 ml) and $NaBH_4$ (0.20 g, mmol). This mixture was heated under reflux for 3 h to give a yellow solution. The solvent was removed *in vacuo* and the residue was extracted with benzene. The benzene solution was filtered and evaporated to dryness. Addition of MeOH gave a yellow powder which was collected by filtration, washed with MeOH and dried *in vacuo*. Yield, 0.21 g. ^{31}P and ^1H spectra indicated that this sample contained 30% of **4** (see above) and 70% of **6** (see below).

Attempts at fractional crystallization of these complexes failed except for an accidental crystallization of **6** over a period of several weeks in an NMR tube; apparently air had leaked through the septum of the NMR tube and selectively decomposed **4**. ReH_3(*rac*-P_4), (**6**): ^{31}P NMR (C_6H_6/C_6D_6): δ 87.8 (s, central PPh); 55.7 (s, terminal PPh_2). ^1H NMR (C_6D_6): δ -7.3 (br, ReH); 0.9–2.2 (m, CH_2); 6.9–8.3 (m, Ph).

2.8 Synthesis of $[ReH_4$(meso-$P_4)]BF_4$ (7)

A solution of **4** (0.10 g, 0.12 mmol) in Et_2O was titrated with $HBF_4 \cdot Et_2O$ to give a white solid. After stirring for an additional 1 h, the colour of the solid changed to light pink. The light pink solid was collected by filtration, washed with Et_2O and dried *in vacuo*. Yield, 0.09 g, 82%. ^{31}P NMR (CH_2Cl_2/C_6D_6): δ 87.9 (s, central PPh); 50.9 (s, terminal PPh_2). ^1H NMR (CD_2Cl_2); δ -6.52 (tt, J(PH) = 20.5, 10.7 Hz, ReH); 1.6–3.1 (m, 12 H, CH_2); 7.2–7.7 (m, 30 H, Ph). Anal. Found: C, 52.93, H, 4.94. $C_{42}H_{46}BF_4P_4Re$ calcd.: C, 53.23; H, 4.98%.

TABLE 1. Crystallographic data for $Re(H_2BEt_2)$(*rac*-P_4)

Empirical formula	$C_{46}H_{54}BP_4Re$
MW	927.8
Crystal size (mm)	0.25 × 0.30 × 0.20
Crystal class	Monoclinic
Space group	$C2/c$
a (Å)	17.651(3)
b (Å)	13.874(2)
c (Å)	17.694(4)
β (°)	102.22(2)
V (Å^3)	4235(3)
Z	4
D_{calc} (g cm^{-3})	1.46
μ(Mo Kα) (cm^{-1})	30.5
F(000)	1880
ω scan width (°)	0.6 + 0.35 tan Θ
Range Θ collected (°) (h, k, l)	1–27 (h $-22 \rightarrow 22$, k $0 \rightarrow 18$, l $0 \rightarrow 22$)
Total no of reflections	5074
Independent reflections	4250
R_{merge}	0.027
No. observed data [$I > 3\sigma(I)$]	3343
Weighting, g	0.003
R	0.028
R_w	0.029
Goodness of fit	1.05
Largest Δ/σ	0.099
Parameters refined	241
Max density in ΔF map (e Å^{-3})	0.57

2.9. X-Ray structure determination of $Re(H_2BEt_2)$(rac-P_4) (5)

Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The ω–2θ scan technique was applied with scan speeds varying from 0.92 to 5.5°/min. The intensities of three standard reflections measured every 2 h showed no decay. An empirical absorption correction was applied [15] (min and max corrections 0.758 and 1.137).

The Re atom was located from a Patterson map and the positions of other non-hydrogen atoms were determined from Fourier and difference Fourier syntheses. The molecule lies on a crystallographic two-fold axis which runs through the Re–B bond. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares to minimize $\Sigma w(F_o - F_c)^2$, where $w^{-1} = \sigma^2(F) + gF^2$. All hydrogen atoms bonded to carbon were positioned on geometric grounds (C–H 0.95 Å) and included in the calculations as riding atoms. An overall hydrogen atom thermal parameter refined to a value of 0.071(3) Å^2. A difference map calculated at this stage revealed the location of the hydrogen bridging between rhenium and boron; this atom was refined with an isotropic thermal parameter. Crystal data, data collec-

TABLE 2. Final positional and thermal parameters for Re(H_2BEt_2)(*rac*-P_4)

Atom	*x*	*y*	*z*	U_{eq} ($Å^2$) [a]
Re	0.0000	0.35640(2)	0.2500	0.028(1)
P(1)	−0.0897(1)	0.3663(1)	0.3320(1)	0.033(1)
P(2)	0.0550(1)	0.4835(1)	0.3264(1)	0.035(1)
C(1)	−0.0817(3)	0.4857(3)	0.3804(2)	0.040(2)
C(2)	0.0047(3)	0.5070(3)	0.4061(3)	0.042(2)
C(3)	−0.0406(3)	0.6026(3)	0.2773(3)	0.052(2)
C(11)	−0.1939(2)	0.3526(4)	0.2926(2)	0.040(1)
C(12)	−0.2183(3)	0.2864(4)	0.2342(3)	0.055(2)
C(13)	−0.2965(3)	0.2718(5)	0.2036(4)	0.073(2)
C(14)	−0.3509(3)	0.3241(5)	0.2300(4)	0.079(3)
C(15)	−0.3288(3)	0.3918(4)	0.2871(4)	0.069(2)
C(16)	−0.2497(3)	0.4074(4)	0.3187(3)	0.056(2)
C(21)	−0.0771(2)	0.2959(3)	0.4236(2)	0.036(1)
C(22)	−0.0049(3)	0.2558(3)	0.4547(3)	0.045(2)
C(23)	0.0083(3)	0.2081(4)	0.5252(3)	0.057(2)
C(24)	−0.0497(3)	0.2001(4)	0.5658(3)	0.058(2)
C(25)	−0.1206(3)	0.2404(4)	0.5365(3)	0.060(2)
C(26)	−0.1343(3)	0.2879(4)	0.4661(3)	0.049(2)
C(31)	0.1561(3)	0.4867(4)	0.3799(3)	0.048(2)
C(32)	0.1808(4)	0.4198(5)	0.4365(3)	0.078(2)
C(33)	0.2562(4)	0.4191(6)	0.4793(4)	0.098(3)
C(34)	0.3082(4)	0.4846(6)	0.4639(5)	0.094(3)
C(35)	0.2866(4)	0.5490(6)	0.4080(5)	0.099(4)
C(36)	0.2102(3)	0.5528(4)	0.3646(4)	0.072(2)
B	0.0000	0.1878(5)	0.2500	0.038(2)
C(4)	0.0547(3)	0.1231(3)	0.2083(3)	0.046(2)
C(5)	0.0128(3)	0.0455(4)	0.1543(3)	0.068(2)
H	0.0447(29)	0.2562(40)	0.2872(31)	0.089(18)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Selected bond lengths and angles for Re(H_2BEt_2)(*rac*-P_4)

Bond lengths (Å)					
Re–P(1)	2.367(1)	Re–P(2)	2.308(1)	Re–B	2.340(7)
Re–H	1.685(52)	B–H	1.345(50)	B–C(4)	1.607(7)
C(4)–C(5)	1.523(7)	P(1)–C(1)	1.856(4)	P(1)–C(11)	1.833(4)
P(1)–C(21)	1.865(4)	P(2)–C(2)	1.847(5)	P(2)–C(3)	1.860(5)
P(2)–C(31)	1.836(4)	C(1)–C(2)	1.526(6)	C(3)–C(3a)	1.548(9)

Bond angles (°)			
P(1)–Re–P(1a)	173.3(1)	P(1)–Re–P(2)	81.3(1)
P(1)–Re–P(2a)	93.6(1)	P(1)–Re–B	93.3(1)
P(2)–Re–P(2a)	80.3(1)	P(2)–Re–B	139.8(1)
H–Re–Ha	68.8(33)	C(5)–C(4)–B	115.1(4)
Re–B–C(4)	123.9(3)	C(4)–B–C(4a)	112.1(5)
H–B–C(4a)	123.0(25)	H–B–C(4)	104.1(24)
H–B–Re	45.1(22)	H–Re–B	34.4(16)
H–Re–P(1)	98.7(20)	H–Re–P(1a)	86.8(20)
H–Re–P(2)	106.8(17)	H–Re–P(2a)	166.6(20)
Re–P(1)–C(1)	109.9(2)	Re–P(1)–C(11)	120.5(1)
C(1)–P(1)–C(11)	103.9(2)	Re–P(1)–C(21)	122.0(1)
C(1)–P(1)–C(21)	94.8(2)	C(11)–P(1)–C(21)	101.6(2)
Re–P(2)–C(2)	111.8(1)	Re–P(2)–C(3)	114.0(1)
C(2)–P(2)–C(3)	99.2(2)	Re–P(2)–C(31)	124.2(2)
C(2)–P(2)–C(31)	100.0(2)	C(3)–P(2)–C(31)	104.0(2)
P(1)–C(1)–C(2)	106.5(3)	P(2)–C(2)–C(1)	110.5(3)
P(2)–C(3)–C(3a)	107.9(2)	P(1)–C(11)–C(12)	118.9(4)
P(1)–C(11)–C(16)	122.6(3)		

tion, and least squares parameters are listed in Table 1. All calculations were performed using SDP [16], SHELX76 [17] and SHELXS86 [18] on a PDP11/23 and an Apollo computer. Final atomic coordinates and thermal parameters are presented in Table 2. Selected bond distances and angles are given in Table 3. An ORTEP diagram of the structure is presented in Fig. 1.

2.10. T_1 NMR data for $ReH_3(dppe)_2$ and $[ReH_4(dppe)_2]Cl$

These complexes were prepared by literature methods [19,20] and their T_1 data were measured as listed in Table 4.

3. Results and discussion

3.1. Rhenium hydride complexes of PP_3

There are several possible routes to the rhenium hydride complexes of the type ReH_3P_4 or $[ReH_4P_4]^+$. Cotton and Luck reported that $ReH_3(PMePh_2)_4$ can be prepared by the reduction of $ReCl_5$ with excess Na in the presence of $PMePh_2$ [21]. We attempted to synthesize $ReH_3(P_4)$ or $ReH_3(PP_3)$ by a similar procedure, but obtained only paramagnetic compounds. Several rhenium hydride complexes (such as $ReH_3(dppe)_2$) can be prepared by the reaction of $ReH_5(PPh_3)_3$ with appropriate phosphines in the absence of solvent at elevated temperature [20]. The

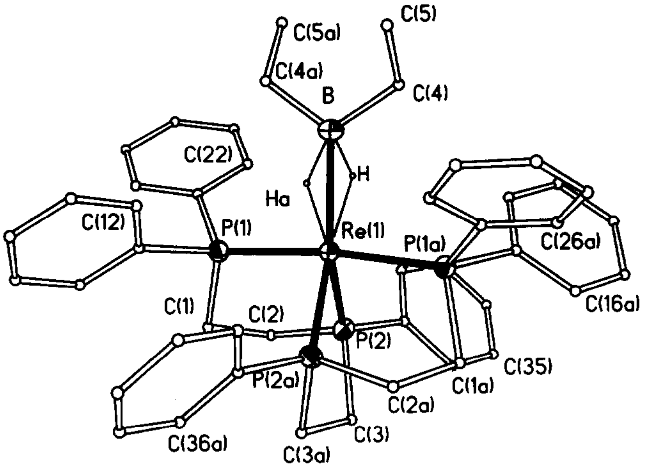


Fig. 1. View of the structure showing the atomic labelling scheme. Thermal ellipsoids are at the 50% probability level. For the sake of clarity, hydrogen atoms bonded to carbon have been omitted and carbon atoms have been assigned as spheres of arbitrary radii.

TABLE 4. ^1H NMR T_1 measurements on the hydride resonances of the rhenium hydride complexes

$ReH_3(dppe)_2$ [a]						
T (°C)	21 [d]	0 [d]	−20	−30	−51	−70
T_1 of ReH_2 [b] (ms)	301	238	194	183	176	204
T_1 of ReH [c] (ms)	301	238	214	182	180	182

$[ReH_4(dppe)_2]Cl$ [e]								
T (°C)	17	−11	−30	−51	−60	−70	−80	−90
T_1 (ms)	213	143	108	75	73	68	71	93

$[ReH_4(PP_3)]BF_4$ [a]						
T (°C)	21	−1	−21	−41	−61	−69
T_1 (ms)	190	155	133	124	137	155

$ReH_3(rac\text{-}P_4)$ [f]							
T (°C)	23	3	−20	−40	−60	−81	−90
T_1 (ms)	152	119	95	61	44	46	66

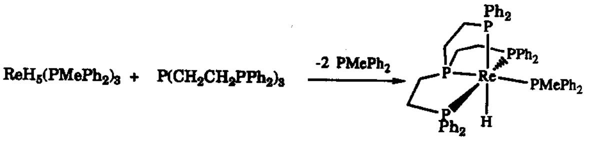
$ReH_3(meso\text{-}P_4)$ [a]						
T (°C)	23 [d]	0 [d]	−20 [d]	−40	−60	−80
T_1 ReH_2 [b]	293	218	173	162	181	325
T_1 ReH [c]	293	218	173	171	166	296

$Re(H_2BEt_2)(rac\text{-}P_4)$ [f]						
T (°C)	22	0	−20	−40	−60	−80
T_1 (ms)	151	129	87	64	51	57

$[ReH_4(meso\text{-}P_4)]BF_4$ [f]							
T (°C)	20	1	−19	−39	−60	−80	−90
T_1 (ms)	206	185	160	145	78	68	88

[a] In CD_2Cl_2 at 400 MHz. [b] T_1 values of the hydride resonance corresponding to two hydrides. [c] T_1 values of the hydride resonance corresponding to one hydride. [d] Only one hydride signal was observed due to fast exchange. [e] In acetone-d_6 at 200 MHz. [f] In CD_2Cl_2 at 200 MHz.

rhenium hydride $ReH_3(dppe)_2$ can also be obtained by using a similar procedure, but starting from $ReH_5(PMePh_2)_3$ [19]. Attempts to prepare $ReH_3(PP_3)$ or $ReH_3(P_4)$ by the reactions of $ReH_5(PMePh_2)_3$ with PP_3 and P_4 were unsuccessful. Thus reactions of $ReH_5(PMePh_2)_3$ with P_4 produced a complicated mixture of rhenium compounds, which were not further characterized. Reaction of PP_3 with $ReH_5(PMePh_2)_3$ gave $ReH(PMePh_2)(PP_3)$ (**1**) (eqn. (1)).



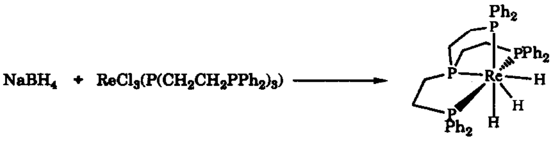
(1)

(1)

The ^{31}P NMR spectrum of the compound displays a broad doublet ($J(PP) = 152.4$ Hz) at 133.6 ppm for the central phosphorus atom *trans* to $PMePh_2$, a pseudo doublet ($J(PP) = 9.1$ Hz) at 42.5 ppm for the PPh_2 *trans* to the hydride, a pseudo doublet ($J(PP) = 14.6$ Hz) at 41.7 ppm for the two PPh_2 of the tetraphosphine that are *trans* to each other, and a doublet ($J(PP) = 152.4$ Hz) at -6.9 ppm for the $PMePh_2$ attached to rhenium. In the ^1H NMR spectrum, the hydride resonance appears at -8.39 ppm as a complicated multiplet. Apparently the tetraphosphine is too small to force the $PMePh_2$ to leave the coordination sphere.

One of the most frequently employed preparative routes to rhenium polyhydrides is the reduction of phosphine halide complexes of rhenium [22]. The green compound $ReCl_3(PP_3)$ has been prepared by King *et al.* by the reaction of $ReCl_3$ with PP_3 in boiling 2-methoxyethanol [23]. Reaction of the green compound $ReCl_3(PP_3)$ with $LiAlH_4$ or $NaBH_4$ did not lead to the hydride $ReH_3(PP_3)$; only paramagnetic material was obtained.

Heating a mixture of $ReCl_3(PMePh_2)_3$ and PP_3 at *ca.* 180°C in the absence of solvent produced a yellow compound that is insoluble in common organic solvents. The yellow compound is likely an isomer of the green compound $ReCl_3(PP_3)$. Unlike the green isomer of $ReCl_3(PP_3)$, the yellow compound can be converted to $ReH_3(PP_3)$ (**2**) by use of $NaBH_4$ (eqn. (2)).



(2)

(2)

The ^{31}P NMR spectrum of the trihydride complex shows a quartet ($J(PP) = 33.7$ Hz) at 156.9 ppm for the central phosphorus atom and a doublet ($J(PP) = 33.7$ Hz) at 68.1 ppm for the terminal phosphorus atoms in benzene at room temperature. The ^1H NMR spectrum for the hydride complex displays a hydride resonance at -6.48 ppm (qd, $J(PP) = 12.7$, 4.0 Hz). Both the ^{31}P and ^1H hydride spectra do not change appreciably with temperature in the temperature range 18 to -80°C, indicating that the molecule is highly fluxional.

Protonation of the trihydride $ReH_3(PP_3)$ by $HBF_4 \cdot Et_2O$ produced $[ReH_4(PP_3)]BF_4$ (**3**) (eqn. (3)).

$$ReH_3(PP_3) + HBF_4 \cdot Et_2O \longrightarrow \underset{\mathbf{(3)}}{[ReH_4(PP_3)]BF_4} \qquad (3)$$

The trihydride is so basic that it can even be protonated by neat MeOH to give $[ReH_4(PP_3)]^+$. The ^{31}P NMR spectrum for the central phosphorus atom appears at 132.8 ppm (q, $J(PP) = 17.2$ Hz) and for the terminal PPh_2 groups at 48.9 ppm (d, $J(PP) = 17.2$ Hz) in acetone. It is interesting to note that both the signals for the central and terminal phosphorus atoms in $[ReH_4(PP_3)]^+$ are shifted *ca.* 20 ppm upfield from those in $ReH_3(PP_3)$. The hydride resonance appears at -6.25 ppm (qd, $J(PP) = 11.7$, 5.1 Hz) in CD_2Cl_2. Like the neutral trihydride complex $ReH_3(PP_3)$, the tetrahydride **3** is highly fluxional as indicated by its variable temperature ^{31}P and ^1H NMR spectra, which do not change appreciably with temperature. The minimum T_1 value for the hydride resonance was measured to be 124 ms at -40°C in CD_2Cl_2 at 400 MHz (see Table 4). It has been observed that the minimum T_1 values for classical rhenium hydrides can be quite short because of rhenium–hydride dipole–dipole relaxation contributions; for example, 96 ms for $ReH_5(PMePh_2)_3$ at 400 MHz in CD_2Cl_2 [24–26]. The method of Desrosiers *et al.* [26] was followed to estimate the closest H–H distance for **3**. First the T_1(min) value is adjusted to 155 ms at 500 MHz (this is a fairly good approximation); this corresponds to an observed relaxation rate, R_{obs}, of 6.45 s^{-1}. Then the contributions from Re ($R_{eH} = 1.91$ s^{-1}) and a maximum of 12 *ortho* hydrogens on phenyl groups ($R_{H(o)H} = 12 \times 0.042 = 0.50$ s^{-1}) are subtracted to obtain a hydride–hydride relaxation rate of 4.04 s^{-1}. The closest distance from a particular hydride to the other hydrides can be estimated as 1.8 Å assuming that two other hydrides are nearest neighbours and one is farther away (for example on the corners of a square). Thus the complex $[ReH_4(PP_3)]^+$ does not contain a dihydrogen ligand. Apparently the rhenium metal centre is too basic to form a dihydrogen complex. Protonation of $Re(H)_3(PMe_2Ph)_4$ and $Re(H)_3(dppe)_2$ also give the tetrahydride complexes $[Re(H)_4(PMe_2Ph)_4]^+$ [27] and $[Re(H)_4(dppe)_2]^+$ (Table 4); the latter complex is calculated from the T_1(min) value of 68 ms at 200 MHz to have pairs of hydrides with the closest separation of 1.7 Å. To be certain that a dihydrogen ligand is present in a $[Re(H_2)H_2L_4]^+$ complex where only the minimum T_1 of the fast exchange hydride resonance is known, the minimum T_1 value would have to be about 21 ms at 400 MHz or 13 ms at 250 MHz, the value measured for the known dihydrogen complex $[Re(H_2)(H)_2(CO)(PMe_2Ph)_3]^+$ at 208 K [28]. The latter complex is more electron-deficient than $[Re(H)_4(PMe_2Ph)_4]^+$, $[Re(H)_4(dppe)_2]^+$ and $[Re(H)_4(PP_3)]^+$.

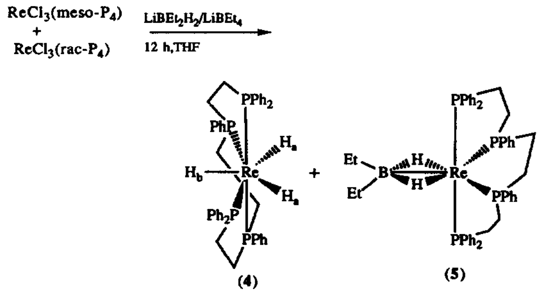
3.2. Rhenium hydride complexes of P_4

Commercially available P_4 reacts with $ReCl_3(PMePh_2)_3$ at *ca.* 180°C in the absence of solvent to give a green-yellowish compound which may be formulated as $ReCl_3(P_4)$.

$$ReCl_3(PMePh_2)_3 + P_4 \xrightarrow{200°;\ 3\ h} ReCl_3(\textit{meso}\text{-}P_4) \text{ and } ReCl_3(\textit{rac}\text{-}P_4) \quad (4)$$

Although this complex is insoluble in common organic solvents, it appears to contain a mixture of complexes containing the *meso*-P_4 and *rac*-P_4 ligands (with the *rac*-P_4 complex in greater abundance), judging from its reactions. It is known that commercial tetraphosphine P_4 is a mixture of the *meso* and *racemic* diastereomers due to the presence of the two asymmetric phosphorus atoms (the central ones) [29]. Thus mixtures of isomeric complexes will be produced when commercial P_4 is used. Even if pure *meso*-P_4 is employed, the same mixture is obtained because the ligand racemizes at the high temperatures required for the reaction with $ReCl_3(PMePh_2)_3$. Hydride complexes could be obtained by reaction of the green-yellowish solid with an appropriate hydride agent (see below). A green compound formulated as $ReCl_3(P_4)$ has been prepared by the reaction of $ReCl_3$ with P_4 in boiling 2-methoxyethanol [23]. However, reaction of the green $ReCl_3(P_4)$ with hydride reagents gave only paramagnetic material instead of the desired trihydride.

Treatment of the green-yellowish $ReCl_3(P_4)$ with "$LiBHEt_3$" [14] in THF produced the rhenium trihydride ReH_3(*meso*-P_4) (**4**) and the novel $BH_2Et_2^-$ complex $Re(H_2BEt_2)$(*rac*-P_4) (**5**) (eqn. (5)).



(4) (5) (5)

The two compounds have different solubility and therefore can be easily separated by recrystallization. The X-ray structure of complex **5** shows that it contains the *rac*-P_4 ligand. It is very likely on the basis of the results presented below and on our experience with analogous osmium chemistry that complex **4** contains the *meso*-P_4 ligand. It appears from this reaction and other reactions outlined below that the starting $ReCl_3(P_4)$ complex contains about 70% $ReCl_3$(*rac*-P_4) and 30% $ReCl_3$(*meso*-P_4); then complex **5** is obtained in 83% yield based on $ReCl_3$(*rac*-P_4) and complex **4** is obtained in 87% yield based on $ReCl_3$(*meso*-P_4). It is important to note that there is no known reaction which interconverts the *meso*-P_4 and *rac*-P_4 isomers once they are coordinated to a metal; the conditions of the reactions below are mild and there is no reason to suspect such an interconversion.

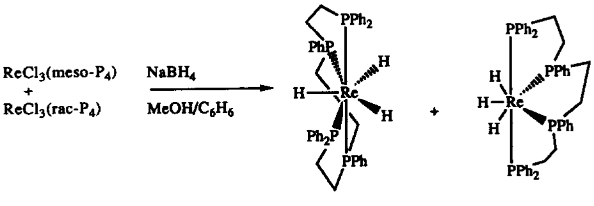
The rhenium trihydride complex ReH_3(*meso*-P_4) (**4**) is a yellow fluxional compound. The hydride resonance is observed at -6.86 ppm (tt, $J(PH) = 17.2$, 5.4 Hz) in C_6D_6 (-7.55 ppm in CD_2Cl_2) at room temperature. The hydride resonance separates into two signals at -7.1 ppm (ReH_b) and -8.1 ppm ($Re(H_a)_2$) when the temperature is below -40°C in CD_2Cl_2 at 400 MHz. The T_1(min) for the hydride resonance of the ReH_2 unit is measured to be *ca.* 162 ms and for the one corresponding to H_b is *ca.* 166 ms in CD_2Cl_2 at 400 MHz. The T_1(min) value for the ReH_2 unit of **4** is similar to that of $Re(H)_3(dppe)_2$ (Table 4) which has an H–H distance of about 1.9 Å. Thus there is no dihydrogen ligand present in **4**. Although the line-shapes of the hydride signals change with temperature, the ^{31}P NMR spectra do not change appreciably with temperatures in the range of 75 to -90°C. Only two singlets are observed throughout the temperature range; at room temperature in benzene the chemical shifts are 100.6 ppm for the central phosphorus atoms and 56.0 ppm for the terminal PPh_2 groups. The absence of observable coupling between the central and terminal phosphorus atoms is unusual. It might be caused by the cancellation of $^2J(PP)$ coupling through Re and the $^3J(PP)$ coupling through the backbone, which are of opposite sign [30–32]. Small $J(PP)$ couplings (< 2 Hz) have also been observed in other complexes containing chelating phosphines which form five-membered rings [30–32].

The ligand *meso*-P_4 forms octahedral complexes in the *cis*-β and *trans* topologies [33]. A study of the stereochemistry of a similar tetradentate ligand containing four arsenic atoms indicates that the *trans* complex is preferred to the *cis*-β complex. The propensity for the *meso*-P_4 ligand to give *trans* and the rac-P_4 to give rhodium complexes with a *cis*-α coordination geometry has also been reported [34]. The osmium dihydrogen complex $[OsH(H_2)(meso\text{-}P_4)]^+$ which is isoelectronic to **4** adopts a *trans* configuration whereas $[OsH_3(rac\text{-}P_4)]^+$ adopts the *cis-α* configuration [8]. The ^{31}P and ^1H NMR data for complex **4** are consistent with a *meso*-P_4 ligand in the *trans* configuration; they would also be consistent with a *rac*-P_4 ligand in the *trans* configuration but this is not possible because the stable form of $ReH_3(rac\text{-}P_4)$ is a *cis* configuration (see below). In contrast to $ReH_3(meso\text{-}P_4)$ where the three hydrides exchanges sites very rapidly above −40°C, the exchange process in $[OsH(H_2)(meso\text{-}P_4)]^+$ is not observed, even at room temperature.

The most surprising feature of the reduction reaction of $ReCl_3(P_4)$ with excess "$LiBHEt_3$" is the production of the novel rhenium complex $Re(H_2BEt_2)(rac\text{-}P_4)$ (**5**). The $BH_2Et_2^-$ originates from an old solution of commercial super hydride "$LiBHEt_3$". Thus a proton coupled ^{11}B NMR spectrum of the super hydride solution in THF displays resonances at −9.7 ppm (br), −16.8 ppm (br) and −17.6 (t, $J(BH) = 68.7$ Hz) versus the reference which is $BF_3 \cdot Et_2O$. The resonances of equal intensity at −17.6 and −16.8 ppm are attributed to $LiBH_2Et_2$ and $LiBEt_4$, respectively. The peak at −9.7 ppm, again of similar intensity to the other two, is likely due to some hydrolyzed product. Fryzuk *et al.* reported that the reaction of $(dippp)PdCl_2$ with commercial $LiBHEt_3$ in THF produced $[(dippp)Pd]_2(\mu\text{-}H)_2 \cdot LiBEt_4$ (dippp = 1,3-bis(diisopropylphosphino)propane) [35]. NMR experiments also suggested that the specific bottle of $LiBHEt_3$ actually contained an equal amount of $LiBH_2Et_2$ and $LiBEt_4$ [35]. Rhenium complexes containing $BH_xR_{4-x}^-$ (x = 1–4) fragments are rare [36]. An η^2-$BH_2R_2^-$ complex has recently been reported for $Cp_3U(HBBN)$ (BBN = 9-borabicyclo(3.3.1)nonane) [37]. Complexes $Cp_2Zr(\eta^2\text{-}BH_2Me_2)H$ and $Cp_2Zr(\eta^2\text{-}BH_3Me)Me$ have been observed as intermediates in the formation of $Cp_2Zr(BH_4)_2$ from the reaction of Cp_2ZrMe_2 with $BH_3 \cdot THF$ [38].

The structure of **5** has been confirmed by X-ray diffraction (see below) and is consistent with the spectroscopic data in solution. The ^{31}P NMR spectrum of **5** in benzene displays two singlets, one at 81.5 ppm for the central phosphorus atom and the other at 51.5 ppm for the terminal phosphorus atom. The ^1H NMR spectrum of **5** in C_6D_6 has a broad hydride resonance at −7.25 ppm corresponding to two hydrogens per rhenium. The T_1(min) value of this resonance of **5** in CD_2Cl_2 was measured to be 51 ms at 200 MHz at −60°C. This is a low value for a classical rhenium hydride complex but is consistent with a hydrogen bridging between boron and rhenium where the boron is the main contributor to the relaxation of the ^1H nucleus. No other signals for hydrogens bonded to boron or rhenium were detected. The chemical shift of the bridging hydrogens is similar to the shift of −6.83 ppm of the Os–H–B hydrogens in the complex $Os(\eta^2\text{-}H_2BH_2)H_3(P(cyclo\text{-}C_5H_9)_3)_2$ [39]. The CH_3 resonance was observed at 0.88 ppm (t, $^3J(HH) = 7.3$ Hz). The compound is static on the NMR time scale. Thus the ^1H NMR spectra do not change with temperature in the temperature range 80 to −80°C. Preliminary data reported for the complex *cis*-$Re(\eta^2\text{-}H_2BH_2)(dppe)_2$ indicated that the bridging hydrides at −9.0 ppm did not exchange positions with the terminal hydrides at 1.27 ppm [40].

Reaction of the green-yellowish $ReCl_3(P_4)$ with $NaBH_4$ in mixed solvents of $MeOH$/benzene produced a mixture of $ReH_3(meso\text{-}P_4)$ (**4**) and another rhenium hydride complex which we tentatively formulated as $ReH_3(rac\text{-}P_4)$ (**6**)



(4) (6)

(6)

Compound **6** has very similar solubility properties to that of **4**; thus it is difficult to separate the two compounds by recrystallization or chromatography. In one experiment, a sample of **6** was obtained by letting a benzene solution of the mixture stand for a week, owing to the decomposition of the trihydride complex $ReH_3(meso\text{-}P_4)$ as oxygen slowly leaked into a capped NMR tube which was initially under N_2. The ^{31}P NMR spectrum for **6** displays a singlet at 87.8 ppm for the central phosphorus atoms and a singlet at 55.7 ppm for the terminal phosphorus atoms in benzene at room temperature. No other resonances are present and this indicates that this sample of **6** is quite pure. The shapes of the ^{31}P NMR resonances do not change appreciably with temperatures between 75 and −90°C. Like the ^{31}P NMR spectra, the ^1H NMR spectra also do not change much with temperature. The hydride resonance was observed as a broad signal at −7.9 ppm in CD_2Cl_2 (−7.3 ppm in toluene-d_8). ^1H integration suggest that there are two hydrides per rhenium. Thus the compound seemed to be $ReH_2Cl(rac\text{-}P_4)$. However, other experiments disprove this formulation. The compound is unreactive to reducing agents such as $NaBH_4$, $LiBHEt_3$ and $LiAlH_4$. Elemental analysis of the "pure sample" mentioned above indicates that only a trace amount of chloride is present in the compound. Thus the compound might be $ReH_3(rac\text{-}P_4)$. Low integration of a polyhydride resonance is common [2,3]. The T_1(min) for the hydride resonance was observed to be 44 ms at −60°C at 200 MHz, which is shorter than those of the other rhenium hydride complexes of Table 4. If it is assumed that the short T_1 of the terminal hydrides in **6** is due to the rhenium, eight *ortho* hydrogens on phenyl and two neighbouring hydrides, then the closest hydride–hydride distance is estimated to be 1.7 Å according to the method of Desrosiers *et al.* [26]. The hydride resonance of the isoelectronic osmium complex $[OsH_3(rac\text{-}P_4)]^+$ has a T_1(min) of 160 ms at 400 MHz [8]; this complex probably has about 1.8 Å for the closest H–H contacts [26]. The T_1 values of **5** and **6** are still larger than those observed for rhenium dihydrogen complexes such as $ReCl(H_2)(PMePh_2)_4$ (25 ms, 200 MHz) [41] and $[ReH_2(H_2)(CO)(PMe_2Ph)_3]^+$ (7 ms, 250 MHz) [28].

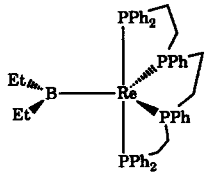
Protonation of $ReH_3(meso\text{-}P_4)$ gave $[ReH_4(meso\text{-}P_4)]^+$ (**7**) (eqn. (7)).

$$ReH_3(meso\text{-}P_4) + HBF_4 \cdot Et_2O \longrightarrow \underset{(7)}{[ReH_4(meso\text{-}P_4)]BF_4} \qquad (7)$$

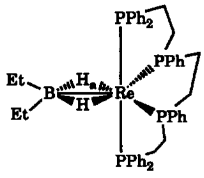
The tetrahydride **7** is highly fluxional like **3**. The ^1H NMR spectrum shows a multiplet at −6.52 ppm (tt, J(PH) = 20.5, 10.7 Hz) in the hydride region in CD_2Cl_2; the four hydrides are apparently equivalent through rapid site exchange. The minimum T_1 value for the hydride resonance (137 ms at −80°C on 400 MHz for **7** in CD_2Cl_2) is smaller than that of the corresponding trihydride complex $ReH_3(meso\text{-}P_4)$ (*ca.* 160 ms), but is still in the range for rhenium trihydride complexes. The ^{31}P NMR resonances were observed at 87.9 ppm for the central phosphorus atoms and at 50.9 ppm for the terminal phosphorus atoms. The slow exchange limit could not be observed in the ^{31}P NMR spectrum, even at −90°C.

3.3. Description of the structure of $Re(H_2BEt_2)(rac\text{-}P_4)$ (5)

The structure of **5** is shown in Fig. 1. Selected bond lengths and angles are given in Table 3. The compound contains a $rac\text{-}P_4$ ligand and an $\eta^2\text{-}BH_2Et_2$ ligand. There is a two-fold symmetry axis along the Re–B bond. The hydrogens on the Re refined as two symmetry-related bridging hydrides, H and H_a (Table 3). The geometry of the coordination sphere, without considering the hydrogen ligands, can be best described as distorted trigonal bipyramidal with P(1) and P(1a) in the axial positions and P(2), P(2a) and **B** in the equatorial plane (structure **A**, refer to Fig. 1 for the labelling of the nuclei).



A



B

In fact, the geometry without considering the hydrides is very similar to that of the five coordinate complex $[ReCl(dppe)_2] \cdot C_6H_5CH_3$ [42]. The bridging hydrides are in a plane defined by H–Re–H_a which is almost in the plane defined by P(2)–Re–P(2a) and approximately orthogonal to the P(1)–Re–P(1a) axis.

There is good evidence for the bridging hydrides. The ^1H NMR evidence has been presented. In addition, the Re–B bond at 2.340(7) Å is the correct length to be bridged by hydrogens. To our knowledge, no structural studies on $Re(BH_xR_{4-x})$ ($x = 1$–4) complexes have been done. However, the Re–B bond length is comparable with the Re–B (hydrogen bridged) distances in $6,6,6,6\text{-}(PMe_2Ph)_3H\text{-}nido\text{-}6\text{-}ReB_9H_{13}$ (r(average) = 2.376 Å) and $2\text{-}(PMe_2Ph)\text{-}6,6,6,6\text{-}(PMe_2Ph)_2ClH\text{-}nido\text{-}6\text{-}ReB_9H_{12}$ (r(average) = 2.357 Å) [43]. In addition the complex $Os(\eta^2\text{-}H_2BH_2)H_3(P(cyclo\text{-}C_5H_9)_3)_2$ has an Os–B distance of 2.30(1) Å [39]. If there were no bridging hydrides present in **5**, then a shorter Re–B distance would be expected. For example the Ir–B distance of the Ir–BBR′ unit (BBR′ = borabicyclo[3.3.1]nonyl) in $fac\text{-}IrH_2(PMe_3)_3(BBR')$ is 2.093(7) Å [44].

The tetraphosphine in **5** adapts a *cis-α* conformation. To our knowledge, X-ray structural studies on only four P_4 complexes of iron group metals exist: $[FeBr(meso\text{-}P_4)]BPh_4$ [45], $trans\text{-}[FeH(N_2)(meso\text{-}P_4)]Br \cdot C_2H_5OH$ [46], $trans\text{-}RuCl_2(meso\text{-}P_4)$ [47] and $[OsH_3(rac\text{-}P_4)]BF_4$ [48]. The last complex has a $rac\text{-}P_4$ ligand in a *cis-α* configuration like **5**. The axial Re–P bond distance (2.367(1) Å) is longer than that of the equatorial one (2.308(1) Å). The Re–P bond distances are normal and are in the range of literature values. For example, the Re–P bond distances range from 2.256(1) to 2.403(1) Å in $[ReCl(dppe)_2] \cdot C_6H_5CH_3$ [42]. The arrangement of the four phosphorus atoms in the complex is quite different from that of other similar ReP_4 complexes such as $ReH_3(dppe)_2$ [49], $[ReH_4(PMePh_2)_4]BF_4$ [27] and $ReCl(H_2)(PMePh_2)_4$ [41]. The difference is due to the presence of tetraphosphine ligand.

4. Conclusions

New neutral trihydride and cationic tetrahydride complexes of rhenium with tetradentate phosphine ligands have been synthesized. The complex Re(H$_2$

BEt_2)(*rac*-P_4) which contains a novel bidentate $BH_2Et_2^-$ ligand was accidentally prepared. The complexes are very fluxional but do not appear to have close H–H contacts. Recent calculations support the idea that late transition metals (on or to the right of the line joining Ru and Ir) are most likely to form dihydrogen complexes [50]. These metals have more contracted d orbitals. The complex $[ReH_4(PH_3)_4]^+$ is predicted to be an eight coordinate tetrahydride which is consistent with our observations [50].

Supplementary material. Tables (SUP-1-5) of complete bond distances, bond angles, anisotropic thermal parameters, and least square planes, calculated hydrogen coordinates (7 pages) and observed and calculated structure factors (12 pages) are available upon request from Robert Morris.

Acknowledgement

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